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CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.

No. V.

ON A NEW OCCURRENCE OF TARTRONIC ACID, WITH SOME REMARKS ON THE MOLECULAR STRUCTURE OF GLYCERIC ACID.

BY SAMUEL P. SADTLER.

(Read before the American Philosophical Society, September 17, 1875.)

In the Propyl series, nine normally formed acids are possible, besides several isomeric unsymmetrically formed ones. They are :—



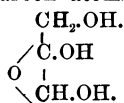
and the following are the acids considered as having the molecular structure just given :—

- I. Propionic Acid.
- II. Lactic Acid (of Fermentation).
- III. Pyruvic or Pyro-racemic Acid.
- IV. Ethylene Lactic Acid.
- V. Glyceric Acid.
- VI. Carbacetoxylic Acid.
- VII. Malonic Acid.
- VIII. Tartronic Acid.
- IX. Mesoxalic Acid.

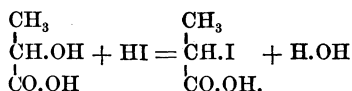
In one or two of these cases however, there is still a difference of

opinion as to whether the acid named is the one possessing the normal molecular structure given above, or is only an isomer of it, having its carbon atoms differently united. Notably with glyceric acid is this yet an open question. Some results lately obtained in the course of a study of this acid appear to me to be of value for the solution of this question.

The other view of the molecular structure of glyceric acid makes it unsymmetrical, two of the carbon atoms being doubly united. The formula given is



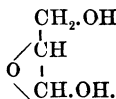
As will be seen, this formula does not contain the Carboxyl group hitherto supposed to be the invariable characteristic of an organic acid. The author of this theory is Prof. Wislicenus, of Würzburg, and the following are the reasons given in support of it. If lactic acid be acted upon with hydrogen iodide, α iodo-propionic acid is formed, according to the following reaction :



This when heated to 150° with strong HI is changed into propionic acid. If, on the other hand, glyceric acid be acted upon with hydrogen iodide, β iodo-propionic acid is formed. If this had the formula



on treatment with moist silver oxide, it would pass into ethylene lactic acid. It does not, however, do this, but a new acid isomeric with ethylene lactic acid is formed—hydracrylic—



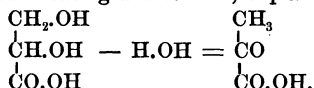
That the molecular structure of this acid is essentially different from that of ethylene lactic acid is proved by the oxydation products of the two. Ethylene lactic acid yields malonic acid, while hydracrylic does not yield a trace of this, breaking up into glycolic and oxalic acids and carbonic dioxide. Moreover, hydracrylic acid on heating yields acrylic acid, a derivative of allyl alcohol, instead of the lactid yielded by the lactic acids.

Prof Wislicenus, however, frankly gives one experiment made by himself, the result of which tends the other way. He reduced the β iodo-propionic acid by sodium amalgam and obtained what appeared to be the normal propionic acid, showing the regular molecular structure.

In favor moreover of the normal structure for the molecule of glyceric acid is the formation of pyruvic or pyroracemic acid



from glyceric acid upon heating this to 140° , explained by the following reaction :



The structure of this pyruvic acid is known from the fact that acted upon by nascent hydrogen it gives normal lactic acid.

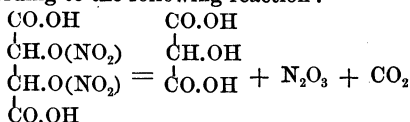
A strong additional argument would be had, if we could show a connection between glyceric acid,



and tartronic acid,



Hitherto tartronic acid had not been formed from glyceric acid, but only in an indirect way, by the spontaneous decomposition of nitro-tartaric acid, according to the following reaction :



However this mode of formation was interesting as tending to show its symmetry of structure. For that matter a dibasic, triatomic acid could hardly exist, except by the assumption of two carboxyl groups.

I have been fortunate enough to find tartronic acid associated with glyceric acid in the oxydation products of glycerine. The preparation of the two acids was as follows: One part by weight of glycerine is mixed with one part of water, and to the mixture is added, by means of a long funnel tube reaching to the bottom of the cylinder, about one and a quarter parts of red fuming nitric acid. After allowing them to rest until all gas evolution has ceased, (which usually takes some six days,) the solution is evaporated down at a gentle heat until the fumes of nitric acid are no longer perceptible. It is then very thick and syrupy. It is now diluted with water, and plumbic carbonate is added in excess. The oxalate and undissolved carbonate are filtered off, and the solution slightly concentrated and allowed to crystallize. The glycerate of lead deposits in thick crystalline crusts. These are separated from the mother-liquor, dissolved, and the lead precipitated out from the solution by sulphuretted hydrogen.

The colorless or light straw-colored filtrate is somewhat concentrated, and calcic carbonate is added to neutralization. The solution is filtered, if necessary, and to the filtrate is added an equal volume of 95 per cent. alcohol. The calcium salts present are all precipitated, in greater part at once, and completely on standing twelve hours.

If the solution had been very concentrated the calcium salt is precipitated in a granular condition. If, on the other hand, it was more dilute, the salt only separates gradually, and has a beautiful micaceous and scaly appearance.

I had at first considered this precipitate to be pure calcium glycerate, but found on dissolving it in water, in order to free it from the lime and obtain the glyceric acid, that while the greater portion dissolved readily in warm water, a considerable portion, although not more than one-tenth of the whole amount, remained and dissolved only on continued boiling. This, when filtered off and washed in cold water, appeared as a dull white almost impalpable powder, contrasting in appearance with the crystalline glycerate.

It was dried carefully at 100° until constant weight was obtained.

Calcium determinations were first made. Weighted portions were ignited in a platinum crucible once or twice with excess of concentrated sulphuric acid until the weight remained constant.

.5755 grms. salt yielded .4925 grms. CaSO_4 equal to 25.22 per cent. Ca.

.1759 grms. salt yielded .1505 grms. CaSO_4 equal to 25.16 per cent. Ca.

The theoretical per cent. of calcium in calcium tartronate is 25.32, while in calcium glycerate, allowing for two molecules of water of crystallization, it is 18.99.

I had analyzed the micaceous preparation of calcium glycerate about the same time and had gotten in two determinations, 14.03, 14.07 per cent. of calcium respectively. The difference was so great that I could not understand it. On reckoning up the molecular weight, however, assuming one atom of calcium to be present, I got 159. The molecular weight of calcium tartronate is 158. Being dibasic, the molecular weight of the calcium compound is of course much less than the weight of the calcium compound of glyceric acid, a monobasic acid.

I endeavored twice to make a combustion of the salt in order to get the per cent. of hydrogen and carbon. Each time calcium carbonate remained undecomposed at the heat of the combustion. I therefore gave them up.

I then took the remainder of my salt, grown rather small, to my great regret, and neutralizing the lime with oxalic acid, obtained the free acid. This, on concentration, deposited out crystals. On examination with a lens they were seen to be of tabular form, well agreeing with the appearance of tartronic acid obtained from nitro-tartaric acid. A combustion was made of these, and here, unfortunately, an accident to the potash bulbs lost me the carbon determination. The hydrogen determination however, is given.

.4348 grms. salt yielded .1323 grms. H_2O equal to 3.33 per cent. hydrogen.

The theoretical per cent. of hydrogen in $\text{C}_3\text{H}_4\text{O}_5$ is 3.33.

An important test that I wished to make but was compelled to forego for the time, was to act upon this tartronic acid with hydrogen iodide. Were its structure symmetrical, it should yield α iodo-malonic acid, which by further treatment with HI or with reducing agents would yield malonic acid.

Wishing to obtain larger quantities of the tartronic acid for further examination, I have since oxydized another portion of glycerine and treated the products in the same way. This time I got no tartronic acid whatever, at least only a trace of calcium salt remained undissolved on heating with water. Evidently here the oxydation had proceeded somewhat differently as no tartronic acid formed. This result is not surprising on reflection, as the oxydation by nitric acid is not capable of much control, and a product once formed is liable to be still further oxydized. Thus glyceric and tartronic acids are both liable to be oxydized into oxalic acid, which always forms in considerable though varying quantity. Indeed the oxydation of glycerine by nitric acid is now known to yield a variety of products, of which, however, no doubt some are secondary ones.

Thus Heintz* has proved that racemic, formic, glycolic, and glyoxalic acids are all found associated with the glyceric and oxalic acids in this product.

The tartronic acid just found, therefore, is only one of several smaller side-products. The known symmetry of structure of the molecules of all these side products, however, certainly argues in favor of a similar symmetry in the glyceric acid molecule.

There is one way of reconciling these two views of the structure of glyceric acid, and that is the assumption of the existence of two isomeric acids, of which one is normal and the other an unsymmetrical acid.

Some results that I have just obtained in purifying the calcium glycerate seem, indeed, to point this way. Should the unsymmetrical glyceric acid preponderate in this mixture, Wislicenus' reactions with hydrogen iodide are readily understood. Another fact, which should not be lost sight of, is that in the decomposition of β iodo-propionic acid by moist silver oxide, Wislicenus† obtained not hydracrylic acid alone, but three other products accompanying it, so that the decomposition was not so simple.

I am now engaged upon a study of this question and hope to be able to give more information upon it, in a short time.

* Ann. der Ch. und Ph. 152, p. 325.

† Ann. der Ch. und Ph. 166, p. 41.